

Thermally poled glass: frozen-in electric field or oriented dipoles?

P.G. Kazansky, P.St.J. Russel

Optoelectronics Research Centre, University of Southampton, Southampton SO9 5NH, UK

Received 25 February 1994; revised manuscript received 24 May 1994

Abstract

Evidence that a frozen-in space charge field causes the appearance of high quadratic nonlinearities in thermally poled glass is obtained from experimental tests of the ratio of nonlinear tensor components and the spatial distribution of the induced $\chi^{(2)}$. A mechanism to explain the fixation of the $\chi^{(2)}$ near the anodic surface is proposed.

1. Introduction

Recently permanent second-order nonlinearities as high as 1 pm/V (~ 0.2 of the value of $\chi_{22}^{(2)}$ in LiNbO₃) have been observed in certain grades of thermally poled commercial fused silica [1]. Such levels of nonlinearity are large enough to be useful for parametric frequency conversion and linear electrooptic modulators, and have therefore excited considerable interest [2-6]. Despite the plethora of poling techniques, the mechanism behind the formation of the second-order nonlinearity is not yet fully understood. During thermal poling in fused silica, samples about 1 mm thick are heated to about 250°C with an applied voltage of about 4 kV, and the second-order nonlinearity is observed only near the anodic surface. It was suggested that a high electrostatic field, appearing in a thin depletion region near the anodic surface, is responsible for this phenomenon [1]. But until now the process by which the $\chi^{(2)}$ is fixed is not clear; it might be caused by orientation of bonds or by the creation of a frozen-in space charge field leading to a dc electronic polarization [7]. A similar question arose in photoinduced second harmonic generation in fibres, and was resolved in favour of the second mechanism in experiments measuring the

ratio of $\chi^{(2)}$ tensor components [8] and the $\chi^{(2)}$ spatial distribution [9].

In the present paper the ratio of $\chi^{(2)}$ tensor components and the $\chi^{(2)}$ spatial distribution in thermally poled glass are experimentally tested. A mechanism for the poling effect, based on the creation of a frozen-in electrostatic field, is proposed.

2. Theoretical considerations

The components of the second harmonic polarization in a glass subjected to a dc electric fields are given by

$$\begin{aligned} P_z &= \epsilon_0 d_{33} E_z^2 + \epsilon_0 d_{31} (E_x^2 + E_y^2), \\ P_y &= 2\epsilon_0 d_{31} E_y E_z, \quad P_x = 2\epsilon_0 d_{31} E_x E_z. \end{aligned} \quad (1)$$

If a space-charge field is the cause of the nonlinearity, the elements of the second-order susceptibility tensor $\chi_{ijk}^{(2)}$ are related to this field via the elements of the third-order susceptibility tensor $\chi^{(3)}$ as follows: $\chi_{ijk}^{(2)} = 3\chi_{ijk}^{(3)} \mathcal{E}_1$. The nonlinear coefficients ($d_{ij} = 2\chi_{ij}^{(2)}$) are related by $d_{31} : d_{33} = 1 : 3$ in transparent isotropic media [10]. If the mechanism is one of dipole orientation, then the ratio of nonlinear coefficients

$d_{31}:d_{33}$ will be 1:3 in a weak orienting electrostatic field ($\mathcal{E} < 10kT/\mu = 4.5 \times 10^{-7}$ V/cm, μ the dipole moment of proton and electron separated at a distance 1 Å, $T = 523$ K) and will depend on the ratio of dipole hyperpolarizability components in a high field ($\mathcal{E}\mu/10kT \gg 1$). It is possible then to rule out a space charge electric-field mechanism if this ratio is not close to 1:3. A ratio of exactly 1:3 will provide support for an electric-field-induced mechanism, while not excluding the possibility of dipole or bond orientation.

In their experiment, Myers et al. [1] measured the ratio of nonlinear coefficients in two slightly different geometries using p-polarized and s-polarized pump falling on the anodic surface of the substrate. They obtained two different values: 1:7 and 1:2. This result was in favour of a model based on dipole orientation.

3. Measurement of the ratio of tensor nonlinear components

We have carried out new measurements of the ratio of the $\chi^{(2)}$ tensor components in an experiment with a simple geometry, where the pump propagates along the thermally poled layer (Fig. 1). We used silica glass samples manufactured by flame fusion of natural quartz (Na concentration was less than 2 ppm, OH concentration was of about 200 ppm). Glass samples about 1.3 mm thick were poled using the standard thermal poling procedure (280°C temperature, 4 kV applied voltage, 20 min poling duration). Q-switched and mode-locked Nd:YAG laser pulses at 1064 nm were used to probe the second order nonlinearity. A 1 mm wide piece was cut from the poled substrate and the two faces parallel to the direction of the applied electric field were polished. The pump beam was focused (the spot size about 50 μ m) into

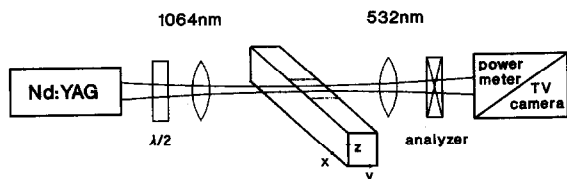


Fig. 1. The geometry used for measurement of the ratio of nonlinear coefficients.

the butt end under the anodic surface of the glass substrate, and the SH power was measured using a power meter and its near-field pattern imaged by means of a microscope objective and a video camera. It should be mentioned that there was no depolarization of pump beam in the sample. Measurements were made for pump polarization both perpendicular (along z axis) and parallel (along x axis) to the nonlinear layer. The ratio of signals was about 4, which suggests a ratio of nonlinear coefficients of about 2. To check this, we analyzed the SH polarization with a Glan polarizer and were surprised to observe that it was elliptical for both pump polarizations. We also observed that the near field pattern of the SH component with polarization parallel to nonlinear layer always consisted two or more lobes (Fig. 2), in contrast to the near-field pattern of the SH component with polarization perpendicular to the nonlinear layer, which was much more uniform. The ratios of tensor components d_{33}/d_{31} , measured with the Glan polarizer tuned for polarization perpendicular or parallel to the nonlinear layer, were respectively 2.9 ± 0.3 and 2.8 ± 0.3 . Each of these values is close to 3 – the value predicted by a model based on built-in space charge field.

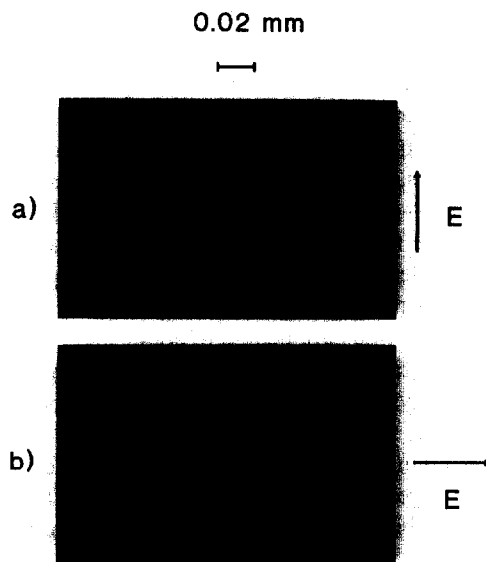


Fig. 2. Second harmonic near-field intensity patterns observed for pump beams polarized (a) perpendicular and (b) parallel to the nonlinear layer; the second harmonic signal is monitored through a polariser orientated in the same direction as the pump electric field.

4. Mechanism of thermal poling effect

On the basis of our experimental results, it is possible to explain the localisation of the nonlinearity near the anodic surface as follows. It is well-known that alkali metal ions (in particular Na^+ because of its high mobility) and H^+ are the main charge carriers in silica glass at temperatures of about 300°C . This is true in spite of the small concentration of these impurities. Recent results indicate the principle role of hydrogen ions in the thermal poling effect [4,11]. Under the action of the voltage applied to the heated glass, these ions will drift to the cathode where most of them are neutralised by incoming electrons, leaving behind a negatively charged depletion region near the anodic surface (assuming zero ionic conductivity at the anode). A high electrostatic field will then appear in the depletion region just below the anode, peaking at the interface. Assuming that all the ions reaching the cathode are neutralised, it is easy to show that in the steady-state the electric field $\mathcal{E}_0$ at the anodic interface, and the depletion region width w , are given by

$$\mathcal{E}_0 = wqN_0/\epsilon, \quad w = \sqrt{2\epsilon V_{\text{app}}/qN_0}, \quad (2)$$

where N_0 is the number density of ions before poling, q their electronic charge, ϵ the dielectric permittivity and V_{app} the applied voltage. After cooling of the sample and removing the electrodes (assuming no

extra charge build-up on the sample surface – such as positive ions attracted from the atmosphere), this field should redistribute itself to yield a zero in the centre of the depletion region. Under these circumstances, the space-charge field cannot be expected to peak consistently at $12\text{ }\mu\text{m}$ below the anodic glass surface, as experimentally observed [3]. If, however, ionization occurs in the high field at the anode surface, electrons could flow into the anode, creating a positively charged layer within the depletion region (see Fig. 3). A large frozen-in electrostatic field will then arise in the region between these two layers. This region is depleted both of cations and electrons, and will therefore have very low thermal conductivity as well as photoconductivity. This picture is confirmed by recent measurements we have made on the sign of the field at different surfaces on the samples. After poling at below 230°C , a negative charge was left behind under the anode, whereas all other surfaces were positively charged. After poling at 280°C , however, the sample was electrically neutral, suggesting that once the depletion region is fully developed (owing to enhanced ionic mobility at the higher temperature), high field ionization occurs.

Our experiments on the measurement of the $\chi^{(2)}$ tensor components provides evidence in support of an electric-field induced $\chi^{(2)}$ model. The existence of “forbidden” field components in the second harmonic signal (i.e., those with polarization *parallel* to

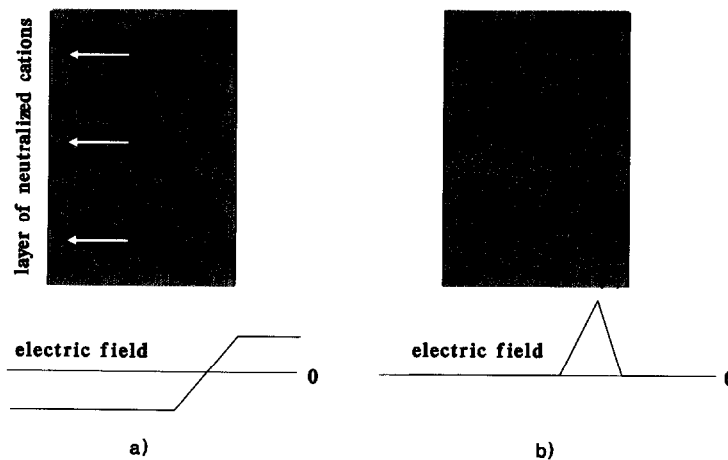


Fig. 3. The proposed mechanism of negatively-charged depletion region formation (a), followed by high field ionization and neutralization (b). The figures represent the situation after the field is turned off and the electrodes removed (the anode was on the right in each picture).

the nonlinear layer for pump light polarised parallel to the layer) can be explained by lateral non-uniformities in the charge distribution. Indeed, components of electrostatic field in the plane of nonlinear layer, pointing in opposite directions at each end of the non-uniform region, must arise and cause highly non-uniform distributions of second harmonic field components polarized in this plane – as observed in the our experiments (Fig. 2). All the components of the electrical field should be taken into account for correct estimation of the ratio of second-order nonlinear tensor components. The “forbidden” electric field components may cause elliptical SH polarization observed in the our experiments and their existence may also explain the difference in the ratios of nonlinear tensor components $d_{31}:d_{33}$ from 1:3 observed in Ref. [1]. The lateral non-uniformities in the charge distribution may be explained by nonuniform distribution of impurities (e.g. OH) in the glass and probably may be illuminated by the proper control of this impurities during glass sample preparation.

5. Conclusions

In conclusion, the ratio of tensor nonlinear components measured by using simple arrangement, when pump propagates along nonlinear layer, was close to the value, predicted by a model based on frozen-in space field, but dipole orientation is not excluded.

Ionization in the high fields near anodic surface can explain the fixing of the induced $\chi^{(2)}$.

Acknowledgements

The work was partly supported by the U.S. Department of the Air Force, through the European Office of Aerospace Research and Development, London.

References

- [1] R.A. Myers, N. Mukherjee and S.R.J. Brueck, *Optics Lett.* 16 (1991) 1732.
- [2] A. Okada, K.I. Ishii, K. Mito and K. Sasaki, *Appl. Phys. Lett.* 60 (1992) 2853.
- [3] P.G. Kazansky, A. Kamal and P.St.J. Russell, *Optics Lett.* 19 (1993) 1141.
- [4] H. Nasu, H. Okamoto, A. Mito, J. Matsuoka and K. Kamiya, *Jpn. J. Appl. Phys.* 32 (1993) 406.
- [5] K. Tanaka, K. Kashima, K. Hirao, N. Soga, A. Mito and H. Nasu, *Jpn. J. Appl. Phys.* 32 (1993) 843.
- [6] A.C. Liu, M.J.F. Digonnet and G.S. Kino, in: *Digest of Conf. on Integrated photonics research* (Optical Society of America, Washington, D.C., 1993), paper PD6.
- [7] N. Mukherjee, R.A. Myers and S.R.J. Brueck, in: *Digest of Conf. on Lasers and electro-optic* (Optical Society of America, Washington, D.C., 1993), paper CThP4.
- [8] V. Mizrahi, Y. Hibino and G. Stegeman, *Optics Comm.* 78 (1990) 283.
- [9] E.M. Dianov, P.G. Kazansky, C. Krautschik, D.S. Starodubov and D. Yu. Stepanov, *Sov. Lightwave Commun.* 1 (1991) 381; 2 (1992) 83.
- [10] S. Keilich, *IEEE J. Quantum Electron.* QE-5 (1969) 562.
- [11] P.G. Kazansky, L. Dong and P.St.J. Russell, *Optics Lett.* 19 (1994) N 10.